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Review

Isolated supramolecules on surfaces studied with scanning tunneling microscopy

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ABSTRACT

To date, supramolecular chemistry is an ever growing research field owing to its crucial role in molecular catalysis, recognition, medicine, data storage and processing as well as artificial photosynthetic devices. Different isolated supramolecules were prepared by molecular self-assembly on surfaces. This review mainly focuses on supramolecular aggregations on noble metal surfaces studied by scanning tunneling microscopy, including dimers, trimers, tetramers, pentamers, wire-like assemblies and Sierpiński triangular fractals. The variety of self-assembled structures reflects the subtle balance between intermolecular and molecule–substrate interactions, which to some extent may be controlled by molecules, substrates and the molecular coverage. The comparative study of different architectures helps identifying the operative mechanisms that lead to the structural motifs. The application of these mechanisms may lead to novel assemblies with tailored physicochemical properties.

1. Introduction

Supramolecular chemistry plays an important role in molecular catalysis, recognition, medicine, data storage and processing as well as artificial photosynthetic devices. In a similar vein, two-dimensional molecular arrays are being investigated on single-crystal surfaces [1–16]. Significant progress has been made in preparing extended networks, a field that has comprehensively been reviewed [1–4]. Bridging the gap between single molecules and molecular monolayers, isolated supramolecular aggregates on surfaces and their physicochemical properties deserve particular interest [17,18].

The formation of supramolecular patterns involves weak, selective and directional non-covalent interactions such as hydrogen bonding (C–H···N [19], O···H–O [20–27]), halogen bonding [28], metal-organic coordination [4] and electrostatic multipole interactions [29,30]. Moreover, van der Waals forces play an important role [31]. Finally, the interaction with the substrate affects the pattern formation, be it in the form of direct molecule–substrate interactions [5,32] or through indirect intermolecular interactions that are mediated by the substrate [33–35].

A number of routes may be chosen to prepare isolated aggregates rather than continuous layers. Controlling the kinetics of nucleation and growth by adjusting deposition rate and temperature, an approach that has been successfully used for atomic adsorbates [36], can be extended to molecules. Patterns of the substrate, *e.g.* the herringbone reconstruction of Au(111) or step patterns on vicinal surfaces [5,32], may be used to confine molecules at low temperatures. Finally, the molecular structure may be designed to favor isolated structures over extended growth.

Below, examples are summarized that have recently demonstrated the above concepts. By choosing substrates, molecular building blocks and coverages, oligomers, wire-like assemblies and fractals have been obtained. Scanning tunneling microscopy (STM)

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has been instrumental in determining the structure of these supramolecular assemblies.

2. Molecular design

2.1. Supramolecular pentamers

Designing suitable molecules appears to be the most natural approach to creating isolated supramolecules. While this is a difficult task in solution chemistry, the presence of a surface further complicates this problem. Molecule–substrate interactions come into play and the intermolecular interactions are modified. In addition, the substrate may mediate new intramolecular interactions through lattice distortion or scattering of surface electronic states [33–35]. Nevertheless, a number of examples can be reported.

Molecules that provide a single attractive site are obvious candidates for the formation of confined structures. Early examples were tetramers and chiral decamers of 1-nitronaphthalin [29,30]. The electrical dipole moment of the molecule and its shape favored the formation of these structures. More recently, all-*trans*-retinoic acid (ReA) was used to prepare supramolecular pentamers on Au(111) (Fig. 1a) [37,38]. The model in Fig. 1b shows that the pentamer is formed *via* cyclic O···H–O hydrogen bonds at the center. At different coverages different numbers of enantiomers were found. Such pentamers were preponderantly observed in the coverage range $0.01\ \mathrm{ML} < \theta < 0.4\ \mathrm{ML}$. In addition to hydrogen bonding, reducing the molecule–substrate interaction is decisive for forming pentamers. This was demonstrated by depositing ReA on the more reactive Ag(111) surface. Using the same preparation conditions as those used for Au(111) no pentamers were observed on Ag. In contrast, on top of a complete ReA monolayer acting as a buffer pentamers did form. Finally the shape of ReA molecule is another key factor for pentamer formation. From *cis*-retinoic acid no pentamers were found, presumably owing to the steric hindrance that arises in forming closed cycles of O···H–O hydrogen bonds [37].

The ReA pentamer is one of the few examples of artificial C_5 symmetric supramolecules on surfaces. Chiral pentamers were previously observed from rubrene on Ag(111) [31]. The pattern formation has been interpreted in terms of repulsive interaction between vertical dipoles, which result from charging of the molecules, and attractive van der Waals interactions at short distance [39]. A particularly intriguing aspect of the rubrene system is the observation of decamers of the supramolecular pentamers (Fig. 2). In addition, the chirality of the original molecular building block is present on both levels, namely pentamers and decamers of perntamers (Fig. 2).

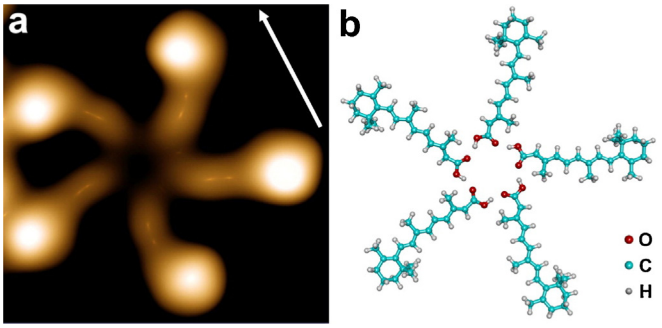

Fig. 1. (a) Image of a ReA pentamer, observed close to a step on Au(111) at an average coverage $\theta \approx 0.2$ ML. In this STM images an arrow indicates a $[1\bar{1}0]$ direction and its length corresponds to 1.5 nm. (b) Optimized geometry of five ReA molecules, confined to a plane. Adapted with permission from Ref. [37] © 2013 American Chemical Society.

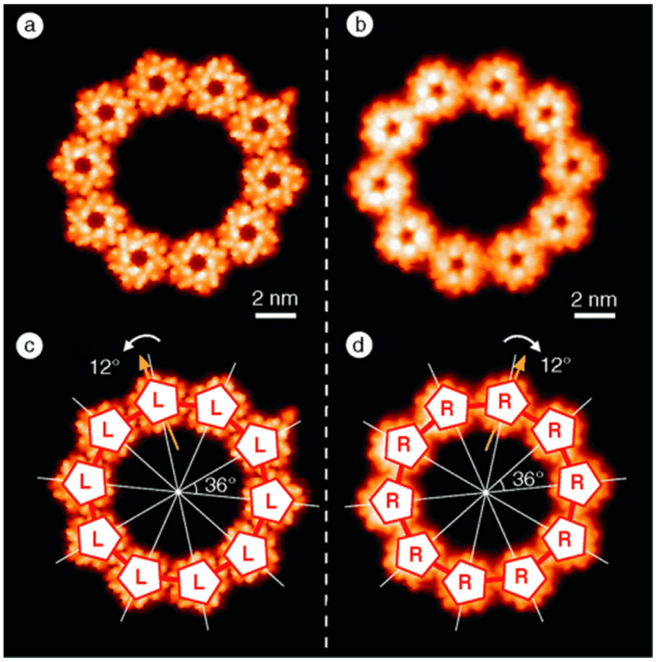

Fig. 2. Formation of chiral supramolecular decagons of pentagonal supermolecules. (a and b) STM images of a left-handed and a right-handed homochiral decagon; (c and d) Construction of the decagons out of ten counterclockwise rotated L-type pentagons and clockwise rotated R-type pentagons. Adapted with permission from Ref. [31]. © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

2.2. Supramolecular dimers, trimers and tetramers

The substituted porphyrin (H2-TBPP) consists of a free-base porphyrin core and four di-tertiarybutylphenyl (tBP) substituents [40]. H2-TBPP molecules are dispersed isolated on Au(111) (Fig. 3a) at low coverages. H2-TBPP molecules exhibit a close-packed arrangement due to van der Waals interaction between the tBP substituents at high coverages (Fig. 3e and i). In a next step (cyanophenyl)-tris (di-tertiarybutylphenyl) porphyrin (CTBPP) was adsorbed [40]. In this molecule a tBP group of H2-TBPP is replaced with a cyanophenyl substituent, bis (cyanophenyl)-bis (di-tertiarybutylphenyl) porphyrin (BCTBPP). The substituent contains two cyanophenyl groups that are substituted at the *cis* position or transposition to ensure the characteristic interaction of the cyano substituents. As shown in Fig. 3b, the majority of CTBPP molecules arrange themselves into trimers, which are located individually at the elbows of the herringbone reconstruction at low coverage [40]. The structural details of the CTBPP trimer are shown in Fig. 3f, while Fig. 3j is a sketch of the proposed cyclic configuration. If the tecton is (phenyl)-tris (di- tertiarybutylphenyl) porphyrin where the cyano substituent is removed from the CTBPP molecule, a random arrangement of the molecules is observed on the surface [40]. Therefore, cyano groups play an important role in the formation of supramolecular aggregation. Fig. 3c shows the supramolecular tetramer comprising four cis-BCTBPP molecules. There are four antiparallel intermolecular connections to form a molecular ring (Fig. 3g and k). Fig. 3d and h shows that supramolecular wires may be formed upon increasing the coverage of trans-BCTBPP (Fig. 3l). There are also antiparallel configurations, and the maximum length of wire exceeds 100 nm [40].

The antiparallel or cyclic configurations of the cyano substituents form those aggregations. The CH···NC contact corresponds to a weak interaction. It is weaker than the interaction encountered in covalent bonds, electronic coupling and energy transfer [41] in biological systems [42,43]. The bulky tBP shape is likely to minimize the molecule–substrate interaction. Consequently, these assemblies